EPR detection of the unstable *tert*-butylperoxyl radical adduct of 5,5-dimethyl-1-pyrroline *N*-oxide: a combined EPR spin-trapping and continuous-flow investigation

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For over 20 years, an EPR spectrum displaying *a*(N), *a*(β–H) and *a*(γ–H) hyperfine splitting constants (hfsc) of ~14.4, ~10.7 and ~1.3 G, respectively, has been attributed to the *tert*-butylperoxyl radical adduct of DMPO. However, essentially identical hfsc have also been reported for the methoxyl radical adduct of DMPO, bringing earlier assignments to the peroxyl radical adduct into serious doubt. Recently, it has been suggested that DMPO/$^{\bullet}$OO^{t}Bu is very unstable and undergoes rapid degradation with the release of free alkoxyl radicals which, through subsequent reactions, yield DMPO/$^{\bullet}$OMe.

In the present investigation, we have generated peroxyl radicals *via* the continuous mixing of *tert*-butylhydroperoxide and Ce(IV) in a micro-flow system, allowing ^{t}BuOO$^{\bullet}$ to be observed directly (Reaction 1).

$$Ce^{4+} + (CH_3)_3COOH \longrightarrow (CH_3)_3COO^{\bullet} + Ce^{3+} + H^{+} \qquad (1)$$

The inclusion of DMPO in the flow system resulted in the appearance of a signal from an unstable ($t_{½} \approx 0.1$ s) nitroxide, with the hfsc values: *a*(N) ~13.8 G, *a*(β–H) ~10.5 G, *a*(γ–H) ~1.3 G. When the flow was stopped, this signal was replaced with a spectrum consisting of signals from a mixture of nitroxides (DMPO/$^{\bullet}$O^{t}Bu, DMPOX and DMPO/$^{\bullet}$OMe), the relative intensities of which depended on the reaction time and reagent concentrations. On the basis of its short $t_{½}$ and the distinction of its hfcs values from those of DMPO/$^{\bullet}$OMe [*a*(N) ~14.3 G, a(γ–H) ~10.8 G, a(γ–H) ~1.3, in this system] the spectrum seen under fast-flow conditions is tentatively assigned to DMPO/$^{\bullet}$OO^{t}Bu.

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